Alkenes

· Alkenes are "unsaturated" hydrocarbons - contain C=C double bond
· General formula for acyclic alkenes is $C_nH_{2n}$
· The simplest example is ethene or ‘ethylene’

Looking down on the molecule

C=C bond length is 133 pm

Each angle is 120°

· All C-H bond lengths (108 pm) are the same
· All H-C-H and H-C-C bond angles (120°) are the same
· C=C bond is composed of one σ-bond and a weaker π-bond (less efficient overlap of orbitals)

Hybridisation:

· Carbon outer shell has one 2s orbital and three 2p orbitals (not equivalent). The s orbital and two p orbitals are mixed together to give three hybrid $sp^2$ orbitals that are equivalent. One p orbital remains unhybridised.
$sp^2$ hybrid orbitals:

Side view  Top view

90°  120°
Formation of carbon-carbon double bonds:

- Two \( sp^2 \)-hybridised C orbitals overlap head-on to form a \( \sigma \) (sigma) bond
- \( p \) orbitals overlap side-to-side to formation a \( \pi \) (pi) bond
- Combination of an \( sp^2 - sp^2 \) \( \sigma \) bond and \( 2p - 2p \) \( \pi \) bond results in sharing four electrons and formation of a carbon-carbon double bond (C=C)
- Electrons in the \( \sigma \) bond are centered between nuclei
- Electrons in the \( \pi \) bond occupy regions above and below the plane

A carbon-carbon double bond: the structure of ethene (ethylene):

\[ \text{sp}^2 \text{ carbon} \] \[ \text{sp}^2 \text{ carbon} \] \[ \text{Carbon-carbon double bond} \]

OVERALL

A double bond has two parts:
- One \( \sigma \)-bond (sp\(^2\) + sp\(^2\) overlap)
- And one \( \pi \)-bond (p + p overlap)

\( \rightarrow \) rotation around the carbon-carbon axis does not occur (requires breaking the \( \pi \)-bond (~128 kJmol\(^{-1}\))

\( \rightarrow \) \( \pi \)-bond electrons are accessible and reactive
NOMENCLATURE OF ALKENES

1. The number of carbon atoms in longest chain including the double bond gives parent.
2. Remove -ane from parent name and add -ene.
3. Numbering priority
   - Give double bond lowest possible number.
     (always 1 and 2 in cyclic compounds)
4. Name substituents as usual.

Constitutional isomers are possible: e.g. C₄H₈
**Double Bond Isomers**

Because there is no rotation about the double bond *stereoisomers* are possible in some cases:

\[
\begin{align*}
\text{CH}_3 & \quad \text{or} \quad \text{CH}_3 \\
m.p. & -139^\circ C \\
b.p. & 4^\circ C
\end{align*}
\]

*(Z)-2-butene*  
(zusammen (same))  
(methyl groups are *cis* to one another)  
* cis-isomer *

\[
\begin{align*}
\text{CH}_3 & \quad \text{or} \quad \text{CH}_3 \\
m.p. & -106^\circ C \\
b.p. & 1^\circ C
\end{align*}
\]

*(E)-2-butene*  
(entgegen (opposite))  
(methyl groups are *trans* to one another)  
* trans-isomer *

These *stereoisomers* differ in the "configuration" (not the constitution) of the atoms in 3D space (i.e. configurational isomers). To have *E/Z*-isomers there must be different groups attached to each end of the double bond:
Double Bond Isomers

- Called **diastereomers** and labeled Z or E

**Rules:**

- Assign priority to each group on each carbon of C=C
  - The higher the atomic number of the atom attached, the higher the priority \( \text{Br} > \text{Cl} > \text{O} > \text{N} > \text{C} > \text{H} \)
  - If identical atoms attached, work along the chain until the first point of difference, then go by atomic number

- If high priority groups on **same** side of C=C  
  \( \rightarrow \) **Z double bond** (German: *zusammen*, same or together)

- If high priority groups on **opposite** sides of C=C  
  \( \rightarrow \) **E double bond** (German: *entgegen*, opposite)

\[
\begin{align*}
\text{CH}_3 & \quad \text{Cl} \\
\text{H} & \quad \text{Br}
\end{align*}
\]

The higher priority groups **are opposite:**

\((E)-2\text{-bromo-2-chloro-propene}\)

\[
\begin{align*}
\text{CH}_3 & \quad \text{Br} \\
\text{H} & \quad \text{Cl}
\end{align*}
\]

The higher priority groups **are on the same side:**

\((Z)-2\text{-bromo-2-chloro-propene}\)
Reactions of Alkenes

• Alkenes undergo a general type of reaction known as addition (extra groups are added).
• The electrons of the $\pi$ bond are available for reaction with certain reagents (A-B).
• The overall effect is the replacement of a $\pi$ bond with a $\sigma$ bond: this is energetically favourable.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
1 \times \pi & + 1 \times \sigma \\
\text{H}_3\text{C} & \quad \text{H} \\
\text{A} & \quad \text{B} \\
2 \times \sigma
\end{align*}
\]
Addition Reactions of Alkenes: Specific Examples

1. **Hydrogenation (addition of hydrogen)**

\[
\text{H} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{C} \quad \text{H}
\]

\[+ \quad \text{H} \quad \text{H} \quad \text{Pd/C} \quad \text{(catalyst)} \]

2. **Halogenation (addition of a halogen)**

\[
\text{H} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{C} \quad \text{H}
\]

\[+ \quad \text{X} \quad \text{X} \quad \text{CCl}_4 \quad \text{(solvent)} \]

\[X_2 = \text{Cl}_2 \text{ or Br}_2 \]

3. **Hydrohalogenation (addition of a hydrogen halide)**

\[
\text{H}_3\text{C} \quad \text{C} \quad \text{CH}_3 \\
\text{H} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{C} \quad \text{H}
\]

\[+ \quad \text{H} \quad \text{X} \quad \text{CCl}_4 \quad \text{(solvent)} \]

\[HX = \text{HCl, HBr, HI} \]

4. **Hydration (addition of water)**

\[
\text{H}_3\text{C} \quad \text{C} \quad \text{CH}_3 \\
\text{H} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{C} \quad \text{H}
\]

\[+ \quad \text{H} \quad \text{OH} \quad \text{dilute H}_2\text{SO}_4 \quad \text{heat} \]
Consider hydrohalogenation (addition of an unsymmetrical hydrogen halide reagent)

- The addition of HX to a *symmetrical* alkene can give only one product:

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} = \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\text{Br}
\]

\[
\text{H}_3\text{C} \quad \text{C} = \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

• The addition of HX to an *unsymmetrical* alkene can give two different products (constitutional isomers):

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} = \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\text{Br}
\]

\[
\text{H}_3\text{C} \quad \text{C} = \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

The major product can always be predicted with MARKOVNIKOV's RULE: The H of the unsymmetrical reagent (H-Br) goes to the C of the C=C bond with the most H's.

**Markovnikov's Rule:** The hydrogen of an unsymmetrical reagent adds to the end of the double bond that has the greater number of hydrogen atoms already attached

To rationalise this we need to consider the MECHANISM of the reaction.
ORGANIC REACTIONS

In organic reactions, electron rich sites in one molecule react with electron-poor sites in another molecule.

Differences in electronegativity of bonded atoms account for electron rich / electron poor sites in molecules.

Electronegativity of Some Common Elements

- The relative electronegativity is indicated
- Higher numbers indicate greater electronegativity
- Carbon bonded to a more electronegative element has a partial positive charge (δ+)

Example:

\[
\begin{array}{c}
\text{δ+} \\
\text{C–OH} \\
\text{δ–}
\end{array}
\]

(Overall electrically neutral)
Organic reactions are classified according to:

1. The **nature of the reagent** which first interacts with the organic substrate *and*
2. The **overall type of process**: addition, substitution, elimination

**Nature of the reagent**: *electrophilic* or *nucleophilic*.

**VERY important definitions:**

\[
\text{Electrophile: A species that seeks an electron pair} \\
\text{Nucleophile: A species that supplies an electron pair}
\]

1. **Nucleophiles**: ‘nucleus loving’, seeks positive things (+ or δ+)
   \[\rightarrow \text{negative (− or δ−) themselves}\]
   eg

2. **Electrophiles**: ‘electron loving’, seeks negative things (− or δ−)
   \[\rightarrow \text{positive (+ or δ+) themselves}\]
   eg
INTRODUCTION TO CURLY ARROW NOTATION

Curly arrow notation is used in organic chemistry as a way of visualising how bonds form and break during the course of a reaction.

A double-headed arrow indicates the movement of a pair of electrons. A curly arrow starts at the electron pair that moves (either a pair of electrons involved in a bond or a lone pair) and ends at the atom to which the electron pair has moved.

Examples

H-O-H → H+ + O²⁻

Electrophile - a species that seeks an electron pair
Nucleophile - a species that provides an electron pair

Curly arrows with ► represent 2 electron in motion.
Curly Arrows

A curly arrow indicates *electron pair* movement.

- A curly arrow *starts* at the electron pair that moves and *ends* at the atom to which the electron pair has moved.

\[
\begin{array}{c}
\text{\includegraphics[width=0.5\textwidth]{curly_arrows.png}}
\end{array}
\]

- Arrow from a bond $\Rightarrow$ bond breaks
- Arrow between two species $\Rightarrow$ new bond formed between them
- Octet rule must be followed (two for hydrogen).
Addition of HX to Alkenes: Electrophilic Addition

• These reactions occur by 2 discrete steps:

starting materials $\xrightarrow{\text{step 1}}$ reactive intermediate $\xrightarrow{\text{step 2}}$ product(s)
(alkene + HX) (organohalide)

Markovnikov's Rule Explained: the major product is formed faster because the reaction intermediate is formed more easily.

Carbocation stability:

- a tertiary alkyl carbocation
- a secondary alkyl carbocation
- a primary alkyl carbocation
- a methyl carbocation
Hydration of Alkenes: *Electrophilic Addition*

Markovnikov's Rule Applies

\[
\begin{align*}
\text{H}_3\text{C} & \quad \xrightarrow{\text{dilute H}_2\text{SO}_4/\text{heat}} \\
\text{H}_2\text{C} & \quad \xrightarrow{} \quad \text{H}_3\text{CCH}_2\text{OH}
\end{align*}
\]